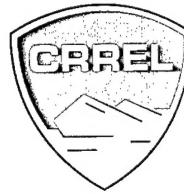


# SPECIAL REPORT

97-12



## Estimating the Total Concentration of Volatile Organic Compounds in Soil A Decision Tool for Sample Handling

Alan D. Hewitt and Nicole J.E. Lukash

April 1997

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**Abstract:** This report describes an on-site method of estimating the total concentration of Volatile Organic Compounds (VOCs) in soil, relative to a site-specific 0.2-mg/kg standard. This decision tool allows on-site sampling activities to incorporate the appropriate soil sample collection and handling protocols required by

different methods of instrumental analysis. Coupling a rapid method for estimating the total VOC concentration with sampling procedures that limit substrate disaggregation and exposure complements efforts to achieve site-representative estimates for vadose zone contamination.

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## PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, and Nicole J.E. Lukash, Physical Science Aid, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory.

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# Estimating the Total Concentration of Volatile Organic Compounds in Soil

## A Decision Tool for Sample Handling

ALAN D. HEWITT AND NICOLE J.E. LUKASH

### INTRODUCTION

Volatile Organic Compounds (VOCs) are the most frequently identified constituents in the designation of environmental hazardous waste (Plumb and Pitchford 1985). Leakage of petroleum fuels from underground storage tanks and improper disposal of spent chlorinated solvents have contaminated large areas throughout the world. Because of the toxicity of many VOCs associated with these products, detection and quantification in all environmental media are of utmost importance. The vadose zone, that region between the ground surface and saturated zone, is a particularly difficult medium to characterize because these contaminants either partially or mainly exist in a vapor phase. Therefore, the vapor phase must be accounted for along with matrix sorbed and liquid phases to achieve an accurate quantitative assessment.

Since the beginning of the cleanup programs mandated by Superfund and the Resource Conservation and Recovery Act (RCRA), gas chromatography/mass spectrometry (GC/MS) Methods 8260 and 8240 (U.S. EPA 1986) have served as the major laboratory procedures for identifying and quantifying VOCs in soils. One of the challenges of coupling a sample collection and handling protocol with this instrumental method of analysis is that GC/MS has a limited range of linear response (two to three orders of magnitude). Typical soil concentrations can range over seven orders of magnitude (percent levels to the current levels of instrumental detection, approximately 0.005 mg/kg). In particular, high analyte concentrations are problematic since they can degrade the performance of the mass spectrometer detection system. To cope with this limitation, samples

thought to be contaminated with VOCs at levels higher than 0.2 mg/kg are prepared by extraction (dilution) in methanol (MeOH), i.e., the high-level method. In contrast, samples thought to have concentrations below 0.2 mg VOC/kg are analyzed using a direct purge procedure, called the low-level method.

A second, and greater, challenge is that VOCs in soil samples fail to maintain their concentration integrity if they are not collected and handled with limited disruption and exposure and if preventive measures are not taken to limit biological degradation of aromatic compounds. It is well recognized that the current protocols recommended in Method 5030 (SW-846, U.S. EPA 1986) often result in a 90% to more than 99% loss of VOCs from soil samples prior to laboratory analysis (Urban et al. 1989, Illias and Jaeger 1993, Lewis et al. 1994, Hewitt et al. 1995, Liikala et al. 1996). To minimize losses through volatilization and biodegradation, in-vial sample collection and analysis Methods 5035 and 5021 have been proposed for the third update of the SW-846. Method 5035 is titled *Modified purge-and-trap and extraction for volatile organics in soil and waste samples*. Method 5021 is titled *Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis*.

For these in-vial methods to be effective, discrete "grab" samples must be transferred directly to vessels with hermetic seals that already contain the appropriate dispersion-extractant solution and preservative for the chosen method of analysis (Hewitt and Lukash 1996). Therefore, samples must be handled differently from the onset of collection, depending on anticipated VOC concentration. This requires that the regulators or

samplers choose in advance which procedure of sample handling is most appropriate for a given site, or samples for both high-level and low-level procedures must be obtained. Previously, users of Method 5030, the procedure cited as being inadequate for preventing VOC losses, collected a bulk soil sample that was then shipped to a laboratory so that subsamples could be removed. Under past circumstances, laboratory personnel often used an olfactory screening method on the bulk sample to establish how the sample would be prepared for analysis.

Proposed Methods 5035 and 5021 use different Volatile Organic-compound Analysis (VOA) vials for their respective automated systems and different sample preparation procedures. Consequently, it will be imperative that the scope of work clearly identify how the samples will be collected and handled, and the specific equipment necessary for their analysis. The laboratories' analytical protocols become an important concern because, if the dispersion-extractant solution is not an organic solvent such as MeOH, the vessel can not be opened to change tops, remove aliquots or introduce surrogates without significant losses of VOCs. This is because, in the absence of a solvent, VOCs quickly partition into the gas phase where they can be readily exchanged with ambient air when the vessel is opened. For this reason it may be best to add surrogate compounds after sample collection via a needle puncture of the septum.

When soils are dispersed in a solvent, such as MeOH, the VOCs are retained as solutes, thus allowing the containers to be opened for the intermittent removal of aliquots without incurring losses (Hewitt 1995). Other advantages of using MeOH are that it is less susceptible to matrix effects (Hewitt et al. 1992, Hewitt 1996b, Askari et al. 1996, Minnich et al. 1996, Hewitt 1997), it allows for multiple determinations per sample, and it is an effective chemical preservative (Hewitt 1995).

Although it is well recognized that in-vial or solvent immersion approaches are necessary for maintaining site-representative VOC concentrations in soil, there continues to be considerable reluctance among regulators to accept the use of MeOH in the field during sample collection activities. Human toxicity, transportation issues (i.e., flammability), and regulatory issues have been cited as reasons for discouraging this practice (Lesnik and Loy 1995). The first reason cited can be addressed by additional precautions in the

work plan, such as special training for field personnel, while shipping constraints can be mitigated by surface transport and reducing the quantity of MeOH contained in a single vessel.

To deal with the regulatory concerns, we recommend the incorporation of a rapid procedure for total VOC analysis at the site. An on-site method of estimating the total concentration of VOCs present vs. a 0.2-mg/kg working standard could be part of a decision tree, providing guidance for subsequent sample preparation and handling. The actual sample preparation and handling could then either be done on-site during the collection or off-site, provided that an adequate transfer device, such as the En Core sampler (En Chem, Inc., Green Bay, Wisconsin) was used (Turriiff et al. 1995, Hewitt and Lukash 1996). With this approach, soil samples from locations where VOCs were anticipated to be less than 0.2 mg/kg would not be placed in MeOH.

Maintaining the representativeness of highly contaminated ( $>1$  mg/kg) soil samples is important because they are often close to the source, i.e., residual or trapped product. Removal or in-situ remediation of this separate or residual phase should receive the highest priority. In contrast, concentrations less than 1 mg VOC/kg can be far removed from sources, particularly when the site has no confining geological features. Moreover, areas where only low level contamination exists will most likely clean up by degradation or diffusion over time, or both, once the source region has been cleaned up.

This report presents a feasibility study for a total VOC decision marker. Our intent is to inform site investigators and regulators of soil sample collection and handling practices that better meet the objective of obtaining representative site information. This will allow effective cleanup strategies to be implemented. When in-vial procedures are coupled with limited disruption and exposure collection techniques, VOCs present as vapor, sorbed, or liquid are included in the measurement (Hewitt 1996a).

## OVERVIEW

Field-portable instruments that measure concentrations of VOCs in the vapor phase within soil samples can be affected by the grain size, porosity, cohesiveness, moisture content, and adsorption capacity of the matrix, and ambient meteorological conditions. Therefore, working standards used to estimate soil VOC concentra-

tions should be site-specific and they must be analyzed under the same conditions as the samples. For practical reasons, instrument response for the 0.2-mg/kg working standard concentration should be at least 10x greater than the background response. Other important criteria are that the technique should be rapid, should require only a small amount of soil, should be easily implemented on site, and should be robust.

In this study, we used a total-VOC analyzer to perform this task. Information concerning the theory of soil vapor analysis with these instruments can be found elsewhere (Fitzgerald 1989, Robbins et al. 1990). The on-site analysis procedure developed here uses a hand-held total-VOC analyzer, takes less than 5 seconds for an analysis, and requires only 10 or 20 g of contaminated soil for most chlorinated and gasoline range organic compounds. Collection and preparation of a soil sample takes less than 1 minute. Proper preparation and analysis of working standards calibrate sample results to both the sample matrix and the existing meteorological conditions, and, depending on the objectives, will allow us to estimate a range of concentrations or test whether concentrations are above or below 0.2 mg VOC/kg. With the exception of a single commercial or laboratory-prepared stock standard, this procedure only requires instrumentation and materials already common to most site investigations, i.e., VOA vials, syringes, and a portable total-VOC analyzer.

## MATERIALS AND METHODS

### Equipment and materials

The total-VOC analyzers used in this study were both equipped with Photo Ionization Detectors (PIDs): the Microtip HL-2000 (Photovac, Inc.) and the Model 580B OVM (Thermo Environmental Instruments, Inc.). The Microtip HL-2000 was modified by replacing the sampling line with a 3-cm-long Teflon tube (3.17 mm o.d.) having a pointed tip. Clear, 44-mL VOA vials were selected as vessels for the working standards and for the analysis of on-site soil vapor samples. We modified the vials by punching a 5-mm-hole in the center of the Teflon-lined silicone septum to allow air to easily pass around the PID sampling line once it was inserted through the hole. To temporarily cover the vials, 3- x 3-cm squares of a light gauge aluminum foil were pressed over the entire rim of the glass vial, then covered with the hole-punched septum and screw cap (Fig. 1). Soil was collected and transferred to these vessels

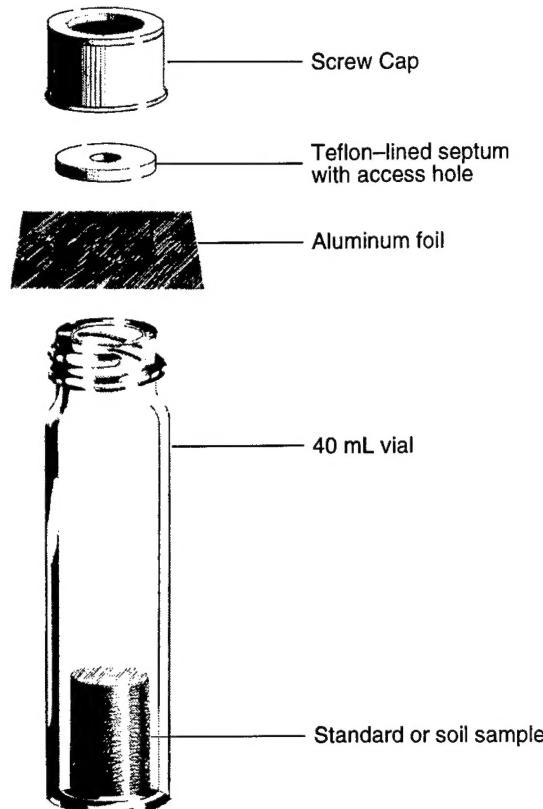


Figure 1. Modified VOA vials for rapid total VOC soil vapor analysis.

with a 10-mL disposable plastic syringe, with the tip, rubber plunger cap, and holding post removed (Hewitt et al. 1995). Reagent grade trichloroethene (TCE), fresh unleaded gasoline, and purge and trap grade MeOH were used to prepare the stock standards. We used a 10- $\mu$ L syringe (Hamilton) to transfer volumes of the stock standard when preparing the working standards.

### Soil vapor analysis

In preparation for a soil vapor analysis, the PID instruments were initially calibrated using zero grade air and standard gas (100 ppm isopropylene) cylinders. To carry out an analysis, soil in 5-g increments (approximate amount transferred when a 10-mL syringe is filled with 3 mL of soil) was transferred to the VOA vial after the cap, septum, and foil liner were removed. Special care was taken when collecting and transferring the soil subsample to minimize disaggregation. Filling the syringe with more than 3 mL of soil is not recommended because larger amounts are often difficult to remove, and are easily disaggregated. Once the appropriate volume of soil was obtained and the foil liner, septum, and cap tightly

secured, the VOA vial was hand shaken for 5 to 10 seconds to disperse the soil. After visually checking the foil liner for adhering clumps of soil (knocked off when present), we analyzed the sample by forcing the sampling line through the foil liner and 3 cm beyond, into the VOA vial. The highest reading displayed by the digital meter within a couple of seconds of the puncturing of the foil liner was the value recorded. The total amount of time between exposing a fresh soil surface and completing this analysis was less than 1 minute.

### Working standards

Separate weighed stock standards of 0.53 mg TCE/mL and 1.1 mg gasoline/mL were prepared by transferring approximately 10 and 40  $\mu$ L of these constituents, respectively, to 25 mL of MeOH. Working standards were prepared by transferring 4  $\mu$ L of these stock standards to VOA vials containing 10 or 20 g of the loam from our site, so as to achieve the desired 0.2-mg VOC/kg concentration. Aliquots of the stock standard were transferred with a 10- $\mu$ L syringe to a clean surface on the inside of the VOA vial. Once capped, with the foil liner and with the hole-punched septum in place, the vials were hand shaken and allowed to sit for at least 2 hours before analysis. The working standards were analyzed using the same procedure as described for soil samples.

## EXPERIMENTS

Experiments were performed to determine the response of the Microtip HL-2000 to working standards of various moisture contents under different meteorological conditions. Initially, we experimented with a native soil. We did a second experiment using the same soil after air drying it and passing it through a 30-mesh sieve, then creating 10 and 20% moisture by weight and water-saturated conditions. These moisture levels were selected for assessing the robustness of the instrumental response for a 0.2-mg TCE/kg working standard. For this robustness evaluation, six replicate 10-g quantities of each soil moisture condition were transferred to VOA vials and spiked with 4  $\mu$ L of the TCE stock standard. In addition, six VOA vials with no soil were spiked. Duplicates of each sample condition (empty, 10%, 20%, and water-saturated) were left at room temperature (23°C), placed outdoors in direct sunlight (35°C), or put in a coldroom (1°C). After waiting

1 hour, we moved the Microtip to each location and allowed it to sit for 15 minutes prior to turning it on and randomly measuring the eight working standards.

In addition to evaluating working standards, we did two separate field trials using field-contaminated soils. One involved near-surface (<0.3 m deep) soil samples. The other was done when two vapor extraction systems were installed. The boreholes for these remediation systems were made with a roto-sonic drill. Samples obtained during this drilling operation extended to depths beyond 30 m. Both of the field trials took place on a site where TCE is the principal contaminant (Hewitt 1994, Hewitt and Shoop 1994, Hewitt et al. 1995).

In the trial involving near-surface sampling locations, the results obtained from the on-site, rapid total soil vapor analysis procedure were compared to results from collocated grab samples, collected using an in-vial procedure that was compatible with equilibrium HS/GC (Hewitt et al. 1992). The sampling locations were flat 20- $\times$  20-cm surfaces, dug with a spade to depths of 10 to 30 cm. At each location, a site-specific working standard was analyzed just prior to the digging of the hole. Immediately after exposing a fresh soil surface, we used two 10-mL syringes to collect the soil for the total VOC vapor analysis. Once the soil vapor analysis was completed, a single syringe was used to collect a collocated sample for HS/GC analysis. The grab samples taken for HS analysis were transferred with a modified syringe directly to 44-mL VOA vials containing 20 mL of Type 1 water (Hewitt et al. 1995). All three collocated soil subsamples were obtained within 5 cm of one another, and on-site analysis and sample collection was completed within 2 minutes of a fresh surface being exposed. At some locations, the same hole was dug deeper for additional sets of samples, without a second (or third) working standard being measured.

Soils taken from the boreholes during the second field trial were either transferred from the drilling auger to a plastic bag or were obtained down-hole in a rigid plastic core liner (1.5 to 3 m length). Samples retrieved after first being transferred to a plastic bag were highly disturbed (disaggregated), while those obtained immediately after the core liners (10-cm diameter) were cut maintained the native soil structure to a much greater degree. Along with the site-specific working standards and VOA vials prepared for the on-site, rapid total VOC vapor analysis, 22-mL VOA

vials were prepared for high- and low-level methods of analysis. Vials containing 10 mL of Type 1 water, acidified with 0.25 g of NaHSO<sub>4</sub>, were prepared for low-level analysis, while ones containing 5 mL of MeOH were prepared for high-level analysis. Grab samples, preserved in MeOH, were analyzed after we transferred a 0.1-mL or smaller volume of the extract to an autosampler VOA vial, containing 10 mL of Type 1 water, for HS/GC analysis. The 22-mL VOA vials used for this procedure, and those prepared for the low-level samples, were compatible with an automated HS/GC analysis system (Hewitt and Lukash 1996). In general, this equilibrium headspace approach is consistent with proposed Method 5021.

For the second field trial, a Model 580B OVM, furnished by the site investigators, was used for on-site total VOC vapor analysis. The working standards were periodically analyzed throughout the day between the collection activities. As with the surface collections, approximately 10 g of soil was analyzed using the rapid soil vapor analysis method. Depending on whether the response was greater or less than that for the 0.2-mg TCE/kg working standard, we transferred grab samples to vials prepared for the high- or low-level methods of analysis.

## RESULTS

Table 1 shows the response of the Microtip HL-2000 to working standards when the VOA vials were either empty or contained 10 or 20 g of the native soil. These working standards were allowed to sit for 2–4 hours or 1–2 days prior to analysis. The instrumental response to the working standards, made with the site-specific soil, was well above the laboratory background readings of 0.5 to 1.0 ppmv. As anticipated, the presence of the soil matrix had a pronounced effect on the instrumental response. The near-surface soil used for these site-specific working standards has a moisture content of 15 ± 5% and an organic carbon content of 1 ± 0.5%. In addition, Table 1 shows the response obtained for working standards that were held for 24 hours or longer prior to analysis. The reduced response for these samples was caused by vaporization losses, since aluminum foil fails to form a hermetic seal with rigid surfaces (Hewitt and Lukash 1996).

The results of the robustness study are shown in Table 2. While not always a factor of 10 $\times$  greater than the background, the responses for the working standards in soil were fairly consistent. The

**Table 1. Microtip readings of TCE and gasoline standards\* in ppmv with and without soil present.**

TCE		Gasoline	
10 g soil <sup>†</sup>	no soil	20 g soil <sup>†</sup>	no soil
10.8	18.7	8.9	17.5
11.1	19.0	8.0	20.4
11.6	19.5	9.3	20.8
11.1	17.8	6.9	21.4
11.0	18.7		
12.1	17.4		
11.3	16.7		
11.0	17.9		
11.5	18.3		
	9.8**		
	10.0**		
	4.3††		
	6.9††		

\* 4  $\mu$ L of stock standards (0.53 mg TCE/mL or 1.1 mg gasoline/mL).

† Weight of soil, thus concentrations were approximately 0.2 mg total VOC/kg.

\*\* Held for 24 hours prior to analysis.

†† Held for 48 hours prior to analysis.

**Table 2. Microtip readings of TCE (ppmv) in working standards\* with and without soils of various moisture contents, under different environmental conditions.**

	<i>In-lab</i>	<i>Direct sunlight</i>	<i>Coldroom</i>
Temperature	23°C	35°C	1°C
Background	1.3	0.0	2.1
No soil	17.7, 17.8	14.8, 14.6	16.2, 16.6
Soil (10 g)			
10% moisture	8.5, 11.0	8.4, 8.4	6.7, 7.4
20% moisture	9.6, 10.5	8.3, 8.1	7.4, 7.2
saturated	11.4, 12.3	8.4, 10.0	10.8, 10.9

\* 4  $\mu$ L of stock standards (0.53 mg TCE/mL).

slightly lower values established for the standards placed in direct sunlight at 35°C may have been caused by pressure buildup and subsequent vapor loss from the VOA vials. There also appears to be a small dependence on moisture content. In general, this method of preparing and using working standards for establishing a decision marker appears only slightly dependent on both soil moisture and the meteorological conditions at the time of analysis.

Tables 3 and 4, respectively, show the results obtained during the first and second field trials, along with values obtained for site-specific working standards for TCE. In the first trial, locations that had been established to be above and below

**Table 3. First field trial results of rapid total VOC soil vapor and collocated grab analyses. In addition, values obtained for the measurement of the site-specific working standards and background are included.**

<i>Soil vapor Microtip PID*</i> (ppmv)	<i>Aqueous HS/GC (mg TCE/kg)</i>	<i>Ratio†</i>
32	0.765	42
1.8	0.0064	—
7.9	0.142	—
64	1.62	40
230	6.75	34
1.8	0.0369	—
1.9	0.0518	—
34	1.28	27
42	1.65	25
0.5	0.0239	—
0.2	0.0422	—
20	1.02	20
120	2.25	53
200	3.50	57
590	11.9	50
$39 \pm 13^{**}$		

Response\* (ppmv) of site-specific working TCE standards and background.

<i>Working standard</i>	<i>Background</i>
8.2	0.6
8.0	0.3
8.3	0.0
6.0	0.0
7.4	0.0

\* Model HL-2000 Photovac (Photovac Inc.)

† Ratio of soil vapor to grab sample concentration, for locations where TCE was >0.2 mg/kg.

\*\* Mean and standard deviation.

the 0.2-mg TCE/kg decision marker were sampled. During the second field trial, all responses were greater than the decision marker. Therefore, during the second field trial, all of the grab samples collected for the analysis were transferred directly to VOA vials containing MeOH.

The relationship between total VOC soil vapor (in ppmv) and collocated grab samples (mg/kg) was both linear and significant, with a correlation coefficient of 0.982 for the first field trial. Indeed, a fairly constant ratio (39±13) existed between these two analyses for the locations where TCE concentrations were greater than 0.2 mg/kg (Table 3). This was not the case for the second field trial because 1) many of the soils sampled were highly disaggregated because of being

**Table 4. Second field trial results of rapid total VOC soil vapor and collocated grab analyses. In addition, values obtained for the measurement of the site-specific working standards and background are included.**

<i>Soil vapor OVM PID*</i> (ppmv)	<i>MeOH HS/GC (mg TCE/kg)</i>
65	9.31
180	11.4
1600	1840
OR†	67.3
OR	1660
1200	51.6
400	10.5
140	1.06
140	7.81
1000	22.9
1900	8560
1900	15200
43	0.14
670	16
530**	5.9
45**	0.66
23**	0.86
130**	1.2

Response\* (ppmv) of site specific working standards and background.

<i>Working standard</i>	<i>Background</i>
6.4	0.0
6.6	0.0
6.9	0.0
5.2	0.0

\* Model 580B OVM (Thermo Environmental Instruments, Inc.).

† OR over range (>2000 ppmv).

\*\* Samples taken from a fresh surface within a rigid plastic core liner.

transferred to a plastic bag, thus often making it impossible to obtain reproducible collocated samples, 2) residual product was intercepted, which is heterogeneously distributed in a porous medium, and 3) the response of the PID is not linear for the high concentrations associated with residual product. The relationship for the first field trial is encouraging, since it indicates that concentrations over a range of at least 0.2 to 10 mg VOC/kg could be estimated using this rapid soil vapor measurement technique, provided that an adequate number (10 to 20%) of confirmation samples were taken. It is probable that this range could be extended to higher concentrations using a field instrument equipped with a flame ionization detector.

## DISCUSSION

Collection of soil for VOC analysis should always be the first operation done after the surface to be sampled has been exposed to the atmosphere. Common sampling locations are soil obtained in core liners or split spoons, pit walls (naturally exposed soil horizons, e.g., river banks), or surface grid points. When a freshly exposed soil surface is not rapidly sampled, analytes existing in a vapor phase diffuse away from this porous matrix, thereby disturbing the temporal equilibrium that existed among the vapor, liquid, and sorbed phases. Following the depletion of the vapor phase, there are nearly instantaneous shifts in the equilibria between the sorbed and aqueous phases (Conant et al. 1996).

We observed an example of how quickly this can happen by tracking VOC concentrations in a soil subsample collected from the middle (1.2 cm below the surface) of a 3.6-cm-i.d.  $\times$  5.1-cm-long split spoon core liner. Grab samples taken from this subsurface location lost more than 90% of the TCE when the core liner was left uncovered in a plastic bag for 40 minutes before sampling (Hewitt and Lukash 1996). In general, as the surface area of exposure increases, the time before there are significant losses decreases, even when precautions are taken to limit native soil structure disruption. Soil texture also has been shown to be a factor. For instance, sandy soils would be expected to lose VOCs more rapidly than cohesive silts and clays (Hewitt et al. 1995). In essence, the extent to which VOCs in a porous medium exist in a vapor state and the rapid shift to this phase upon disruption are the principal factors controlling the success of a rapid analysis technique for soil vapor.

In addition to exposure concerns, soil samples must be transferred directly to vessels with their hermetic seals that either contain a solvent or permit an analysis to be done without being opened. Proposed Methods 5035 and 5021 both recommend the use of VOA vials with Teflon faced silicone septa for in-vial sample handling and analysis when VOC concentrations are below 0.2 mg/kg. For concentrations above 0.2 mg/kg, however, neither method in the initial draft provides guidance on how to handle samples without incurring large volatilization losses. Instead, they defaulted to the past procedure of filling a bottle with a bulk soil sample

and removing a subsample after the bulk sample reached the laboratory. The steps involved with filling, storing, and removing soil contaminated with VOCs all have been shown to be susceptible to volatilization and in some cases biodegradation losses (Hewitt et al. 1995). Losses of VOCs from soil samples with high levels of contamination can be limited, however, by transferring them directly to vessels containing MeOH (Urban et al 1989, Hewitt 1994).

To avoid placing samples with VOC levels less than 0.2 mg/kg in MeOH, this study has demonstrated a simple method of preparing site-specific working standards and field samples so that they can be rapidly analyzed on-site. Tables 1 and 2 show that the performance of working standards was reproducible and acceptably insensitive to typical soil moisture and meteorological conditions. Trends in these initial findings, however, suggest that working standards should be prepared within 8 hours (or less) of their use, and that they should be stored in a cool location and out of direct sunlight. Of perhaps greatest importance is our finding that the relationship between total VOC soil vapor and collocated grab sample analyses can be very significant. For instance, the linear relationship shown in Figure 2, which is for all measurements obtained during the first field trial, has a correlation coefficient ( $r$ ) of 0.982. Over the concentration range shown in Figure 2, the response of the PID appears linear; however, at higher concentrations, we anticipate that this relationship would become nonlinear. Most likely this linear range would be expanded for higher concentrations if hand-held flame ionization detectors were used.

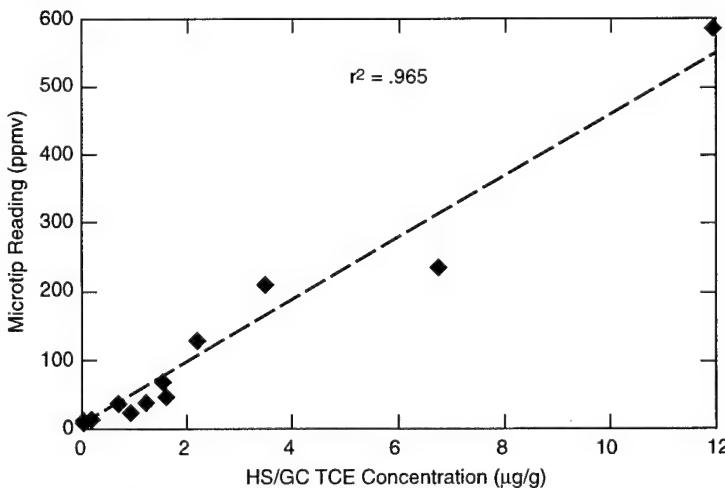


Figure 2. Relationship between rapid total VOC soil vapor analysis and grab samples for the first field trial.

This feasibility study only considered field samples contaminated with TCE. However, other compounds would be expected to behave similarly, since the response of PIDs varies by less than a factor of 1.4 for many common chlorinated and aromatic hydrocarbons (i.e., TCE, tetrachloroethene, benzene, and toluene). Furthermore, it is possible that this on-site rapid analysis method would also work for fuels heavier than gasoline, although the reduction of highly volatile constituents may require larger quantities ( $\approx 50$  g) of soil. We encourage regulators and site investigators to incorporate this on-site systematic and rapid approach to soil vapor analysis, so that informed decisions about how to handle and prepare samples for VOC analysis can be made. To assist in the documentation of a standard operational procedure, a general outline of this method is provided in Appendix A.

## SUMMARY

In general, low-concentration-level methods are practical when we attempt to establish the full spatial extent of the impact of a spill or leak of VOCs into the vadose zone. However, when the main objective of a site investigation is to locate and remediate source regions, where residual product often exists, methods that maintain the representativeness of high levels of VOC concentrations ( $>0.2$  mg/kg) in soil samples are of paramount concern. Failure to maintain representative VOC concentrations results in false negative levels and often prolongs the investigation stage, and can lead to inadequate remediation, and possibly even a premature site closure. To address these shortfalls, we recommend estimating the total VOC concentration at a sampling location before collecting samples for accurate quantitation. The approach described here was successfully applied during two field trials at a site contaminated with TCE, and should also be effective for most other halogenated and aromatic compounds, including petroleum products. This method will tell site investigators when the use of MeOH is justified for on-site sample preparation by indicating when VOC concentrations exceed 0.2 mg/kg.

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## APPENDIX A: FIELD METHOD FOR RAPID SOIL VAPOR VOC ANALYSIS\*

### I. Summary

*A. Analytes:* This method is suitable for estimating the vapor concentration of VOCs in the field using battery-operated equipment.

*B. Matrix:* This method is suitable for the estimation of total VOC concentration in unsaturated and saturated soil.

*C. General Method:* A 10-g (or larger) subsample of contaminated soil is manually dispersed within a capped VOA vial with aluminum foil liner and hole-punched septum. A soil VOC vapor determination is made by piercing the foil liner with the sampling line of a total-VOC analyzer. Comparison of the analyzer response to a 0.2-mg/kg site specific working standard (same volume of soil as sample) to that of the sample serves as a decision marker for how a collocated grab sample should be handled and prepared for laboratory VOC analysis.

### II. Site-specific Working Standard

A working standard is prepared using the contaminant-free site-specific soil and the VOC(s) of interest. The instrumental response to the working standard at the 0.2-mg total VOC/kg concentration should be at least 10 $\times$  above the normal background reading. To achieve this separation in instrumental response, different volumes of soils will be necessary for different analytes and their mixtures. For this study, 10 g was used for TCE and 20 g for gasoline. A 4- $\mu$ L aliquot of the respective stock standard (0.53 mg TCE/mL or 1.1 mg gasoline/mL) was transferred to VOA vials containing soils to make the working standards. Working standards should be prepared and used daily.

### III. Apparatus and Chemicals

1. Field-portable, battery-operated total VOC analyzer with a photo ionization detector and calibration gas cylinders.
2. Clear glass 44-mL VOA vials with aluminum

foil liners and hole-punched septums (slightly larger than o.d. of analyzer sampling line).

3. 10-mL plastic syringes with their tips, rubber plunger cap, and holding post removed.
4. 10- $\mu$ L syringe.
5. Stock standard containing analytes of interest diluted in MeOH. Note: A 1-mL volume would be sufficient for the preparation for more than 200 working standards.

### IV. Procedure

Once an undisturbed soil surface is exposed for sampling, 10-mL plastic syringes are used to transfer 5-g plugs of soil to a VOA vial. After capping with an aluminum foil liner and hole-punched septum, disperse the soil by hand shaking for 10 to 15 seconds. Total VOC vapor is then analyzed, after quickly checking for soil aggregates adhering to the foil liner, by shoving the analyzer's sampling line through this barrier. The maximum instrumental response obtained within seconds of piercing the foil liner is compared to the typical response obtained for the site-specific 0.2-mg total VOC/kg working standards.

In accordance with the protocols recommended by the SW-846 manual (U.S. EPA 1986), when the total VOC vapor response of the sample is greater than that of the working standard, a collocated 5-g sample should be transferred with a subcorer (syringe) directly to a vessel containing 10 mL of MeOH. If the response of sample is less than that of the working standard, then a previously selected low-level in-vial procedure should be used.

Performing a total vapor analysis and collecting a collocated grab sample from within the same soil horizon and vicinity (5 cm) should take less than 2 minutes. However, in addition to minimizing the exposure period, care must also be taken to limit soil structure disaggregation and contacting of the soil transfer device with the solution, if present, in the collection vessels.

\* AEC protocol format.

# REPORT DOCUMENTATION PAGE

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